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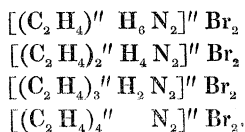
XVI. "Researches on the Phosphorus-Bases."—No. XII. Relations between the Monoatomic and the Polyatomic Bases.
By A. W. HOFMANN, LL.D., F.R.S. Received August 17, 1860.

In recording my experiments on the derivatives of triethylphosphine, I have had more than one opportunity of alluding to the energy and precision which characterize the reactions of this compound. The usefulness of triethylphosphine as an agent of research has more particularly manifested itself in the study of the polyatomic bases, the examination of which, in continuation of former inquiries, was naturally suggested by the beautiful researches on the polyatomic alcohols published during the last few years. In the commencement these studies were almost exclusively performed with reference to derivatives of ammonia; but the results obtained in the examination of triethylphosphine have, in a great measure, changed the track originally pursued, and of late I have generally preferred to solve the problems which I had proposed to myself, by the aid of the phosphorus-bases.

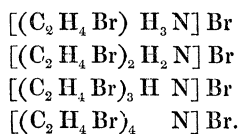
The light which the study of these compounds throws upon the nature of the polyatomic bases generally, will be fully appreciated by a retrospective glance at the deportment of triethylphosphine under the influence of dibromide of ethylene, and a comparison of the products formed in this reaction with the results suggested by theory.

A simple consideration shows that the action of diatomic bromides upon bases must give rise to the formation of several classes of compounds. Let us examine by way of illustration the products which may be expected to be formed in the reaction between ammonia and dibromide of ethylene.

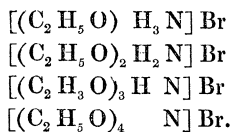
The diatomic bromide being capable of fixing two molecules of ammonia, we have in the first place four diatomic bromides of the formulæ



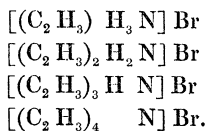
These are, however, by no means the only salts which, in accordance with our present conception of diatomic compounds, may be formed in this reaction. Taking into consideration the general deportment of dibromide of ethylene, there could be no doubt that, under certain conditions, this body would act with ammonia as a monoatomic compound, giving rise to another series of bodies, in which the hydrogen would be more or less replaced by the monoatomic molecule $C_2 H_4 Br$, viz.



Further, if the reaction took place in the presence of water, it was to be expected that the latent bromine of these salts, wholly or partially eliminated in the form of hydrobromic acid, would be replaced by the molecular residue of water, and thus, independently of any mixed compounds containing simultaneously bromine and oxygen, a series of salts might be looked for, in which a molecule $C_2 H_4 (HO) = C_2 H_6 O$ would enter monoatomically.



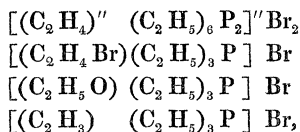
Lastly, remembering the tendency exhibited by ethylene-compounds to resolve themselves in the presence of alkalies into vinyl-products, it appeared not improbable that a fourth series of bodies would likewise be formed,



In the experiments on the action of dibromide of ethylene upon ammonia, which I have already partly published, and which, in a more connected form, I hope soon to lay before the Royal Society, I have not, indeed, met with the whole of these compounds; but in the place of the deficient members of the groups new products have made their appearance, whose formation in the present state of our

knowledge could scarcely have been predicted, and thus the problem of disentangling the difficulties of this reaction becomes a task of very considerable difficulty. Nor did the action of dibromide of ethylene upon ethylamine, diethylamine, and triethylamine, which I subsequently studied, afford a sufficiently simple expression of the transformations suggested by theory. The difficulties disappeared at once when the experiment was repeated in the phosphorus-series. In the reaction with dibromide of ethylene, the sharply-defined characters of triethylphosphine exhibited themselves with welcome distinctness, and in consequence more especially of the absence of unreplaced hydrogen—whereby the formation of a large number of compounds of subordinate theoretical interest was excluded—the general character of the reaction, the recognition of which was the object of the inquiry, became at once perceptible.

I have shown that the action of dibromide of ethylene upon triethylphosphine gives rise to the formation of four different compounds, viz.



each of which represents one of the *four* groups of compounds, which under favourable circumstances may arise from the mutual reaction between ammonia and dibromide of ethylene, the production of a greater number of terms being impossible on account of the ternary substitution of triethylphosphine.

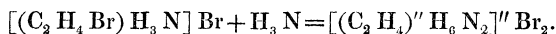
Whilst going on with the researches on the phosphorus-bases which I have taken the liberty of submitting to the Royal Society, in notes sketched as I advanced, I have not altogether lost sight of the experiments in the nitrogen-series, which had originally suggested these inquiries. Numerous nitrogenated bases, both mono-atomic and diatomic, with which I have become acquainted during this investigation, must be reserved for a future communication. I may here only remark, that these substances, although differing in several points, nevertheless imitate in their general deportment so closely the corresponding terms of the phosphorus-series, that the

picture which I have endeavoured to delineate of the phosphorus-compounds, illustrates in a great measure the history of the nitrogen-bodies.

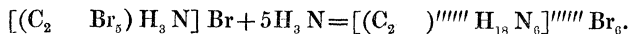
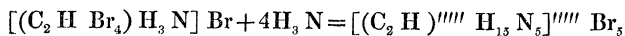
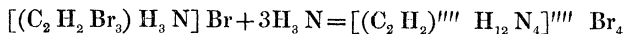
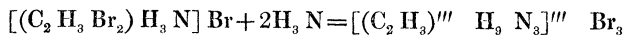
In conclusion, a few words about the further development of which the experiments on the polyatomic bases appear to be capable, and about the direction in which I propose to pursue the track which they have opened.

Conceived in its simplest form, the transition from the series of monoatomic to that of diatomic bases, may be referred to the introduction of a monochlorinated or a monobrominated alcohol-radical into the type ammonia, the chlorine and bromine thus inserted furnishing the point of attack for a second molecule of ammonia.

If in bromide of ethylammonium—to pass from the phosphorus-series to the more generally interesting nitrogen-series—we replace 1 equiv. of the hydrogen in ethyl by bromine, we arrive at bromide of bromethylammonium, which fixing a second equivalent of ammonia, is converted into the dibromide of ethylene-diammonium, the latent bromine becoming accessible to silver-salts.

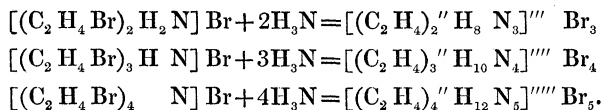


The further elaboration of this reaction indicates two different methods for the construction of the polyatomic bases of a higher order. In the first place, the number of ammonia-molecules, to be incorporated in the new system, may be increased by the gradually advancing bromination of the radical. By the further bromination of ethyl in bromide of bromethylammonium and the action of ammonia on the bodies thus produced, the following salts may be generated:—



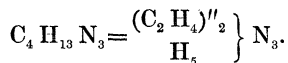
Again, the fixation of the ammonia-molecules may be attempted, not by the progressive bromination of the ethyl, but by the accumulation of monobrominated ethyl-molecules in the ammonium-nucleus. The bromide of di-bromethylammonium, when submitted to the action of ammonia, would thus yield the tribromide of a triammo-

nium ; the bromide of tri-bromethylammonium, the tetrabromide of a tetrammonium ; and lastly, the bromide of tetrabromethylammonium, the pentabromide of a pentammonium.



As yet the bromination of the alcohol-bases presents some difficulty ; appropriately selected reactions, however, will doubtless furnish the several brominated bases. They may probably be obtained by indirect processes, similar to those by which years ago I succeeded in preparing the chlorinated and brominated derivatives of phenylamine ; or these bodies may be generated by the action of pentachloride or pentabromide of phosphorus upon the oxethylated bases, a process, which, to judge from the few experiments recorded in one of the preceding sketches, promises a rich harvest of results.

I have but a faint hope that I may be able to trace these new paths in the numerous directions which open in a variety at once tempting and perplexing. Inexorable experiment follows but slowly the flight of light-winged theory. The commencement is nevertheless made, and even now the triammonium- and tetrammonium-compounds begin to unfold themselves in unexpected variety. One of the most remarkable compounds belonging to the triammonium-group is *diethylene triamine*,



This base, *the first triacid triammonia*, forms splendid salts of the formula



which will be the subject of a special communication.